#### TECHNICAL MEMORANDUM

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RE: Monsanto Soda Springs Site 913-1101.605

Contaminant Transport Modeling Following Cessation of Plant Production Well Pumping

## INTRODUCTION

The purpose of this memorandum is to present an assessment of the potential changes in groundwater quality at the Monsanto Soda Springs site following cessation of Plant Production Well pumping. In particular, the objective of the work is to evaluate whether groundwater quality in the southeastern corner of the Monsanto site could exceed risk-based standards for cadmium, fluoride, manganese, nitrate and selenium if the production wells cease operation.

## SITE BACKGROUND

The Record Of Decision (ROD) established groundwater remediation goals for five constituents of concern at the Monsanto site: cadmium, fluoride, nitrate, selenium and manganese. These remediation goals are the Maximum Contaminant Levels (MCLs) under the Safe Drinking Water Act for all constituents with the exception of manganese (Table 1). The manganese limit is a risk-based concentration. Table 1 summarizes the remediation goals.

TABLE 1

Remediation Goals for Constituents of Concern (COCs)

Constituent of Concern (COC)	Remediation Goal (mg/L)
Cadmium (Cd)	0.005
Fluoride (F)	4
Nitrate (as N) /or as (NO <sub>3</sub> )	10/44
Selenium (Se)	0.05
Manganese (Mn)	0.18

The following three significant historic source areas were identified during the RI: the Underflow Solids Ponds, the Northwest Pond and the Old Hydroclarifier. The Northwest Pond and the Old Hydroclarifier are located to the east of the Monsanto Fault and the Underflow Solids Ponds are located to the west. Remedial measures have been implemented at each historic source area. The monitoring wells associated with each source area are listed in Table 2.

TABLE 2
Source Area Monitoring Wells

Source	Upper Basalt Zone Wells (UBZ)	Lower Basalt Zone Wells (LBZ)
East of Monsanto Fault		
Northwest Pond	TW-16	TW-18
	TW-17	
Old Hydroclarifier	TW-40	TW-44
West of Monsanto Fault		
Underflow Solids Ponds	TW-37	TW-45

Recent groundwater monitoring data from each of the source area wells was evaluated to determine the magnitude and extent of exceedences to the remediation goals. For each source well, constituent concentrations from the last three annual sampling events (1999, 2000 and 2001) were averaged and compared to the remediation goal. The results of this evaluation are summarized in Table 3. Constituents that exceed the remediation goal are highlighted in bold type.

TABLE 3

Source Area Monitoring Well Concentrations

Monitoring	Aquifer	Consti	tuents of Co	ncern Aver	age Concent	rations <sup>a</sup>
Well	(Upper			(mg/L)		
	or Lower	Cadmium	Fluoride	Nitrate	Selenium	Manganese
	Basalt)			(as N)		
Remediatio	on Goal	0.005	4	10	0.05	0.18
UBZ Backs	ground	0	0.4	4	0	0.02
Concentr	ation					
(Golder, 1	1985) <sup>b</sup>					
Northwest Pon	ıd					
TW-16	UBZ	0.57	2.7	5.3	0.25	0.001
TW-17	UBZ	0.003	2.3	0.02	0.004	2.0
TW-18	LBZ	0.0004	0.4	0.01	0.002	0.4
Old Hydroclar	ifier					
TW-40	UBZ	2.1	5.1	13	0.93	0.1
TW-44 LBZ		0.04	0.8	0.5	0.03	0.2
Underflow Solids Ponds						
TW-37	UBZ	0.39	12	7.2	0.36	0.7
TW-45	LBZ	0.006	0.8	0.02	0.001	0.5

<sup>&</sup>lt;sup>a</sup>Average concentration calculated from last three sampling events (1999, 2000 and 2001). Non-detect values assumed equal to half the detection limit in statistical calculations. Bolded values exceed the remediation goal.

Cadmium, selenium and manganese concentrations in the aquifer below the Northwest Pond currently exceed the remediation goal. Cadmium exhibits the greatest exceedence at two orders of magnitude above the remediation goal. Beneath the Old Hydroclarifier, all constituents exceed the remediation goals.

Monsanto operates three production wells to supply process water and one production well to supply potable water to the Soda Springs plant. All four wells are located on the east side of the fault. PW-4 is located upgradient of the Old Hydroclarifier and the Northwest Pond. The pumping rates assigned in the groundwater model (Golder, 2002) based on information provided by Monsanto and information contained in the RI are as follows:

<sup>&</sup>lt;sup>b</sup>Background concentrations determined from wells TW-28, TW-29 and TW-2 (nitrate and manganese background concentrations not reported in 1985 report).

- PW-1: 900 gpm;
- PW-2: 660 gpm;
- PW-3: 1,000 gpm; and,
- PW-4: 300 gpm.

Table 4 summarizes estimated annual mass removals for each of the production wells located downgradient of the source zones. These calculations assume a constant continuous pumping rate. Production well concentrations applied in mass removal calculations are the average of measurements from 1999, 2000 and 2001.

TABLE 4
Pumping Well Mass Removals

¥47.a11	Pumping Rate	Production Well Concentration <sup>a</sup>				Production Well Annual Mass Removal					
Well	Kate	Cd	Se	NO <sub>3</sub>	Mn	F	Cd	Se	NO <sub>3</sub>	Mn	F
	gpm		mg/L					kg/year	ı		
PW-1	900	0.047	0.052	4.4	0.004	0.81	84	93	7,878	7	1,450
PW-2	600	0.004	0.013	4.4	0.004	0.63	5	17	5,777	5	827
PW-3	1,000	0.003	0.009	3.9	0.005	0.51	6	18	7,759	10	1,015
Total	2,500	-	-	-	-	1	95	128	21,414	22	3,292

<sup>&</sup>lt;sup>a</sup>Average concentration calculated from last three sampling events (1999, 2000 and 2001). Non-detect values assumed equal to one half the detection limit in statistical calculations.

## CONTAMINANT FATE AND TRANSPORT

The migration of solutes in groundwater is controlled by advection, mechanical dispersion, retardation, and diffusion. Diffusion is generally a slow process, and in areas of high groundwater flow velocities such as the Monsanto aquifer, the effect of diffusion on solute concentrations is generally masked by the effect of groundwater movement. Dissolved constituents are transported with the groundwater flow (advective transport). Differences in groundwater velocity along a flow path as well as variable flow path lengths result in dispersion. Dispersion (or mixing) results in a decrease in solute concentration. Dispersion occurs in both the direction of groundwater flow (longitudinal dispersion) and in directions normal to the groundwater flow path (transverse horizontal and transverse vertical dispersion).

The transport of solutes in groundwater may also be retarded during transport due a number of reactions and processes including sorption and chemical and biological reactions. The process by which a solute becomes distributed between the groundwater and the aquifer materials is partitioning. A partition, or distribution coefficient (K<sub>d</sub>) describes the partitioning of a constituent between the aquifer material and groundwater. Solutes may also chemically precipitate onto the aquifer matrix.

Where the partitioning of a constituent is described by a distribution coefficient, the retardation ( $R_f$ ) of the contaminant front relative to the bulk mass of water is described by the retardation factor where:

$$R_f = 1 + \rho_b/n * K_d$$
 (Equation 1)

Where:

 $\rho_b$  is the bulk mass density; n is the porosity; and,  $K_d$  is the distribution coefficient.

Because distribution coefficients are dependent on a number of variables including pH, adsorbent, adsorbate concentration (e.g. aluminum iron/oxide concentration, clay content, organic matter content) and presence/absence of competitive ions, they are site specific. In the absence of site specific K<sub>d</sub>s, literature values are often applied. The wide range in values reported in Table 5 reflects these variations.

TABLE 5

Literature COC Partition Coefficients

	Literature	Literature Partition Coefficients (ml/g)				
Constituent	Batelle (1989) <sup>a</sup>	Dragun (1988) <sup>b</sup>	EPA (1999) <sup>c</sup>			
Cd	14.9	1.3 - 27	8 – 4,000			
F	F 0 -		-			
Se	5.91	1.2 – 8.6	-			
		Se(IV)				
NO <sub>3</sub>	0	-	-			
Mn	16.5	0.2 – 10,000	-			

<sup>&</sup>lt;sup>a</sup> pH range of 5 to 9, <10% adsrobent (clay, organic matter and aluminmum oxyhydroxides)

<sup>&</sup>lt;sup>b</sup> Kd ranges for soils and clays.

<sup>&</sup>lt;sup>c</sup> pH range of 5 to 8, ionic strength <0.1 M), humic material concentration <5 mg/L, no organic chelates (e.g. EDTA), oxidizing conditions

<sup>&</sup>quot;-" indicates value not reported.

The EPA cadmium K<sub>d</sub> range reported in Table 5 is the result of a literature survey. A total of 174 values were compiled including the following ancillary information where available (number of samples for which this information was available provided in parentheses): clay content (62), pH (174), cation exchange capacity (CEC) (22), total organic content (63), dissolved cadmium concentration (172) and aluminum/iron-oxide data (16). Linear regression analyses were performed to establish relationships between these parameters and K<sub>d</sub>. The highest correlation (R=0.75) was noted between pH and log (K<sub>d</sub>). The regression equation is provided below. It should be noted that due to scatter in the data, at any given pH, K<sub>d</sub> values may vary by 2 orders of magnitude.

$$Log (K_d) = -0.55 + 0.45 (pH)$$
 (Equation 2)

## Mobility of Constituents of Concern

The mobility and potential retardation mechanisms for each of the COCs is discussed below. Conclusions regarding contaminant mobility from the 1985 Hydrogeologic Investigation are then discussed (Golder, 1985).

#### Fluoride

Fluoride exists in the –1 valence state. In calcareous soils and sediments, fluoride concentrations may be controlled by the mineral fluorite (CaF<sub>2</sub>). Fluoride is not strongly adsorbed by soils; however, adsorption is greatest at pH values between approximately 4 and 6.5. Fluoride forms strong complexes with aluminum (EPRI, 1984).

#### Cadmium

Cadmium exists in the +2 valence state. It is adsorbed by oxides of aluminum, iron and manganese and also by calcite. The adsorption edge for cadmium occurs at a higher pH than that of Pb, Cu and Zn (EPRI, 1984). In groundwaters, otavite [CdCO<sub>3</sub>] precipitation may control cadmium concentrations. Review of three widely accepted geochemical databases (WATEQ, PHREEQC and MINTEQA2) indicates a range of solubility constants for otavite from 10<sup>-13.74</sup> to 10<sup>-12.1</sup>.

## Selenium

In nature, selenium can exist in four valence states: -2, 0, +6 and +4. In oxidized waters at neutral pH, selenium will exist as an anion. Selenium (+6) will be predominantly present as SeO<sub>4</sub><sup>2-</sup> and Se(+4) will be present as HSeO<sub>3</sub>. Above approximately pH 7.6, Se(+4) is predominantly present as SeO<sup>2-</sup>. Selenate (Se+6) species are considered quite mobile, especially in alkaline conditions. Selenite (Se+4) species are significantly less mobile. Reducing environments favour the formation of elemental Se and selenide (-2).

Elemental selenium is insoluble. Selenide, which forms sparingly-soluble minerals such as FeSe<sub>2</sub> and FeSe, is immobile in most aquifers.

Selenium will adsorb to both aluminium and iron hydrous oxides and amorphous aluminosilicates. Because selenium exists as an anion in solution, maximum selenium adsorption occurs at low pH, reducing its mobility. Selenium (+4) is reported to adsorb more strongly to hydrous iron oxides than Se(+6). The opposite behaviour has been observed for clay minerals, that is, Se(+6) is more strongly adsorbed than Se(+4). Sulfate has been reported to compete with selenium for adsorption sites (EPRI, 1984).

#### Nitrate

Nitrate is very mobile in groundwater and is transported in groundwater systems with little or no retardation (Freeze and Cherry, 1979).

## Manganese

Manganese may exist in five valence states +2, +3, +4, +6 and +7. Manganese mobility is redox dependent, exhibiting greater mobility under reduced as opposed to oxidized conditions. Under oxidizing conditions, aqueous manganese concentrations may be reduced by the precipitation of oxides and hydroxides. Manganese concentrations may also be controlled by the precipitation of rhodochrosite [MnCO3] (EPRI, 1984).

## Constituent Mobility at the Monsanto Site

The 1985 Hydrological Investigation (Golder, 1995) concluded that fluoride, chloride and sulfate are transported conservatively at the Monsanto site. Retardation of selenium and cadmium was observed, with cadmium retarded to a greater degree than selenium.

The 1985 Hydrological Investigation evaluated the potential for fluorite [CaF<sub>2</sub>] as a secondary mineral control on groundwater fluoride concentrations. Review of reported solubility constants for fluorite indicated a wide range of variability from  $10^{-11.09}$  to  $10^{-9.79}$ . Following discussions with geochemical specialists and researchers actively working in the area and review of saturation indices for the Monsanto site, Golder adopted a solubility constant of  $10^{-9.79}$ . Site groundwaters were generally found to be oversaturated with respect to fluorite in 1985. It was reported that fluorite equilibrium should be reached in a period of weeks to several months on site. Golder concluded that fluorite had potentially precipitated in the UBZ beneath the Underflow Solids Ponds southwards to the southern boundary of the site. Fluorite may also have precipitated in the UBZ downgradient of the Northwest Pond and the Old Hydroclarifier. The degree and extent however is unknown (Golder, 1985).

The Hydrological Investigation (Golder, 1985) concluded that site groundwaters were undersaturated with respect to cadmium carbonate (otavite). This study applied a solubility constant of  $10^{-11.19}$ , as reported in the WateqF and Wateq2 databases. Review of other databases (MINTEQA2, PHREEQC), indicates a range of reported solubility constants. Figure 1 illustrates cadmium solubility as a function of pH for three solubility constants. These curves were generated using PHREEQC and the solution composition of TW-20 from May 2001. This figure illustrates minimum otavite solubility above pH 8. Between pH 6 and 8 (the typical range of groundwater pH at the Monsanto site), otavite solubility declines. A decrease in the log K of otavite from  $10^{-11.19}$  to  $10^{-13.7}$  results in approximately a two order of magnitude decline in aqueous cadmium concentrations.

## CONTAMINANT TRANSPORT MODEL APPROACH AND RESULTS

A GoldSim<sup>1</sup> model was developed to simulate groundwater transport of the five constituents of concern. Model development followed the steps listed below. Each of these steps is described in detail in subsequent sections.

- Groundwater Flow System Definition The groundwater flow system
  was defined using the results of the post-closure groundwater flow
  model developed in MODFLOW. The model was used to determine the
  groundwater flow directions and groundwater velocity when the plant
  production wells are turned off.
- 2. <u>Estimation of Source Zone Contaminant Loading</u> Current contaminant loading to the Upper Basalt Aquifer (UBZ) from the Northwest Pond and the Old Hydroclarifier was estimated from source zone well monitoring data. Current concentration trends were evaluated to estimate future loading.
- 3. <u>Determination of Site Specific Kd Values</u> Contaminant mobility west of the Monsanto fault was evaluated to estimate site-specific partitioning coefficients that could be applied to predict contaminant mobility elsewhere on the stie. Partition coefficients were assigned to each contaminant.
- 4. <u>Contaminant Transport Simulation</u> Contaminant transport accounting for retardation and dispersion was simulated. Contaminant concentrations at the point of compliance were predicted and compared to remediation goals.

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<sup>&</sup>lt;sup>1</sup> www.goldsim.com

## **GoldSim Model Input Parameters**

## **Source Zone Loading**

Current and future contaminant loading from the Old Hydroclarifier and Northwest Pond were assigned based on monitoring data from wells at each source location. For the Old Hydroclarifier, monitoring data from TW-40 was evaluated. For the Northwest Pond, data from both TW-16 and TW-17 were evaluated and loading rates were assigned based on the well yielding the highest contaminant concentration. As TW-16 is the shallower well of the two, this well generally yielded the highest concentrations. The one exception was manganese whose concentration was higher in TW-17. Higher manganese in this well is attributed to more reducing conditions at depth in the basalt aquifer.

Concentration trends for each source well were evaluated to predict future loading trends. As shown in Figure 2, contaminant concentrations in the Northwest Pond source well (TW-16) generally declined between 1984 and 1992. Since 1992, concentrations of most constituents have been generally stable. Manganese is the one exception. Manganese concentrations in TW-17 currently demonstrate an increasing trend. For all constituents but manganese, source zone concentrations for input to the GoldSim model were determined by averaging the monitoring results from the last three sampling events (1999, 2000 and 2001). Because manganese concentrations are currently increasing, the maximum observed manganese concentration was assumed.

Monitoring results for the Old Hydroclarifier source well (TW-40) are shown in Figure 3. Between 1984 and 1995, constituent concentrations in TW-40 generally declined. Between 1995 and 1996 however, constituent concentrations generally increased. Since 1996, most constituent concentrations have either remained relatively stable or declined slightly. The one exception is selenium, which since 1996 has demonstrated an increasing trend. For all constituents but selenium, source zone concentrations for input to the GoldSim model were determined by averaging the monitoring results from the last three sampling events (1999, 2000 and 2001). Because selenium concentrations are currently increasing, the maximum observed selenium concentration was assumed.

Table 6 summarizes source zone concentrations for both the Northwest Ponds and the Old Hydroclarifier.

### TABLE 6

GoldSim Source Zone Concentrations

Constituent of Concern (COC)	Assigned Source Zone Concentration <sup>a</sup> (mg/L)		
	Northwest Pond	Old Hydroclarifier	
Cadmium	0.6	2.1	
Fluoride	2.7	5.1	
Nitrate (as N)	5.3	13	
Selenium	0.25	1.1	
Manganese	2.2	0.1	

<sup>&</sup>lt;sup>a</sup>Bolded values exceed the remediation goal.

Source zone concentrations were assumed constant over the entire 30-foot UBZ aquifer depth. Source zone areas were as follows:

Northwest Pond: 470 feet by 900 feet; and,
Old Hydroclarifier: 128 feet by 128 feet.

## <u>Cadmium Source Zone Concentrations</u>

Although the 1985 Hydrological Investigation concluded that otavite [CdCO<sub>3</sub>] was not likely controlling cadmium concentrations at the Monsanto site, speciation modeling conducted as part of this study indicates that otavite may be supersaturated in some locations.

Figure 4 superimposes TW-40 cadmium concentrations versus pH on the otavite solubility curves presented earlier. This plot illustrates a general trend of decreasing cadmium concentrations with increasing pH. A number of the sample points lie close to the uppermost solubility curve, suggesting this curve may be appropriate for the Monsanto site. If source zone cadmium concentrations are indeed being controlled by otavite solubility, provided the pH of Monsanto groundwater does decline, current measured cadmium concentrations should be indicative of future trends.

Similar plots for source zone wells TW-37 and TW-16 are shown in Figures 5 and 6. These plots do not illustrate a decline in cadmium concentrations with pH. If the uppermost curve is indeed the solubility limit at the Monsanto site, otavite is generally undersaturated at these sources. These plots would suggest dissolution of otavite solubility is not controlling source zone concentrations at these wells.

## **Basalt Aquifer Properties**

#### <u>Partition Coefficients</u>

To estimate site-specific partition coefficients for the constituents of concern, contaminant mobility west of the Monsanto Fault was evaluated. The major source of contamination west of the fault is the Old Underflow Solids Ponds. These ponds received underflow solids between 1963 and 1983. In 1987 these ponds were capped. Wells TW-37, TW-22 and TW-24 screened in the Upper Basalt Zone monitor source concentrations. Well TW-37 is located approximately 430 meters (1,400 feet) upgradient of TW-22 and TW-24. Because groundwater flow west of the Monsanto Fault is not influenced by pumping wells, groundwater in this area advects under a natural gradient. Constituent travel times were estimated by evaluating arrival times in downgradient wells.

The mobility of chloride was first evaluated as this constituent is generally regarded as conservative, that is to say it is transported at the rate of groundwater flow. Although chloride concentrations are affected by physical processes (dispersion and diffusion), which serve to reduce the peak concentration downgradient of the source, it is not affected by chemical reactions (e.g. adsorption or mineral precipitation) that retard transport. Chloride concentrations in TW-37 declined from a peak of 275 mg/L (1985) following capping of the source. Since 1995, chloride concentrations have remained relatively stable at ranging from 25 to 40 mg/L. Chloride concentrations in TW-22 followed a similar trend. The peak concentration on record in this well was 313 mg/L. Chloride concentrations are currently relatively stable at 100 mg/L.

The estimated arrival time for the core of the chloride plume at TW-20 and TW-39 (located along the south plant fence line) is between 1992 and 1993. Assuming the source was released in 1973 (mid-point of pond life), the core of the chloride plume took approximately 20 years to travel from TW-37 to TW-20 and TW-39, a distance of approximately 1,220 meters (4,000 feet). This equates to a groundwater velocity of 61 meters/year (200 feet/year). The peak chloride concentration at TW-20 and TW-39 was 190 mg/L.

The core of the chloride plume is estimated to have arrived at TW-53 (located south of the plant fence line) in 1994. The peak concentration at this well was 125 mg/L. Therefore the core of the chloride plume took 21 years to travel from TW-37 to TW-53, a distance of approximately 1,490 meters (4,900 feet). This equates to a groundwater velocity of 71 meters/year (233 feet/year), which is in agreement with the first estimate. The peak chloride concentration at TW-53 was 120 mg/L.

Table 7 compares source zone chloride concentrations to peak concentrations measured downgradient.  $C/C_0$  values are shown as an indication of the effects of dispersion on peak chloride concentrations.

## **TABLE 7**

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	Sou	ırce		Fence	e Line			of Fence ne
Constituent	TW-37 (mg/L) (C <sub>o</sub> )	TW-22 (mg/L)	TW-20 (mg/L)	C/C <sub>o</sub>	TW-39 (mg/L)	C/C <sub>o</sub>	TW-53 (mg/L)	C/C <sub>o</sub>
Chloride	275	310	190	0.7	185	0.7	120	0.4
Cadmium	1.2	0.07	0.02	0.02	0.03	0.03	ND	-

Constituent mobility relative to chloride was evaluated for selenium and cadmium by comparing concentration hydrographs for each contaminant to chloride.

## Selenium

Selenium monitoring data is available from 1991 to present. Because the monitoring record for this constituent is truncated, peak source zone concentrations cannot be determined. Since 1991, selenium concentrations in the source wells TW-22 and TW-37 have followed the same trends as chloride. Comparison of chloride and selenium trends at TW-20 and TW-53 suggests that selenium is transported conservatively in the basalt aquifer. This statement assumes that selenium measured at a concentration of 0.74 mg/L in 1992 is representative of the core of the selenium plume.

### <u>Cadmium</u>

The maximum measured cadmium source concentration at TW-37 was 1.2 mg/L. Since capping in 1987, cadmium concentrations at the source have declined following a similar trend to that of chloride. Between 1992 and 2001, cadmium concentrations remained relatively constant at 0.4 mg/L. Cadmium concentrations in source well TW-22 are lower than TW-37. Over the entire period of record, cadmium concentrations in TW-22 have remained below 0.07 mg/L. Currently cadmium in this well is relatively stable at 0.03 mg/L. Cadmium concentrations in TW-24 are currently approximately equal to TW-37 at 0.3 mg/L.

The core of the cadmium plume has not yet reached the fence line wells. Cadmium concentrations in TW-20 and TW-39 have remained below 0.03 mg/L. Cadmium is below detectable limits in TW-53 over the period of record.

Without data on cadmium concentrations between the source (TW-37) and TW-20 and TW-39, the degree of cadmium retardation cannot be quantified. A minimum retardation value however can be calculated on the basis that the cadmium plume has not yet reached TW-20 in the 28 years following release (1973 to 2001). The velocity of

the cadmium plume is therefore less than 44 meters/year (140 feet/year). This equates to a minimum retardation value of 1.4. Applying Equation 1 assuming a porosity and bulk density of 0.25 and 2055 kg/m $^3$  for the basalt aquifer, results in a minimum  $K_d$  of 0.05. Comparison of this value to those presented in Table 5 indicates that this is indeed a minimum estimate. In the absence of a site-specific  $K_d$  value, literature values were applied in the model.

The cadmium  $K_d$  was represented by a log normal distribution. The minimum, maximum and geometric mean values of the distribution were 1.3 ml/g, 27 ml/g and 6.7 mg/g, respectively (Dragun, 1988).

## **Hydraulic Transport Parameters**

## Groundwater Velocity and Porosity

Groundwater flow velocity was based on the results of groundwater flow modeling (Golder, 2002). Porosity was assumed to range from 0.2 to 0.3, with a most likely value of 0.25. Porosity was represented by a triangular distribution in GoldSim.

## **Dispersivity**

Dispersivity generally increases with distance and is therefore a scale dependent property. This trend is shown in Figure 7, a plot of longitudinal dispersivity values for a range of aquifer conditions compiled by Gelhar *et al.* (1985). As a general rule, longitudinal dispersivity is approximately 10% of the distance traveled (Appelo and Postma, 1994) as shown by the "best fit" curve drawn in Figure 7. A dispersivity value of 10% of the path length was applied in the Phase II Investigation Remedial Study (Golder Associates, 1995). This value was also applied in this study. Transverse horizontal and transverse vertical dispersivity are generally a fraction of longitudinal dispersivity. In this study, transverse vertical and horizontal dispersivity were assumed equal to 1% and 0.1% of longitudinal dispersivity.

To confirm that the applied transverse dispersivity values were reasonable, dispersion of the chloride plume west of the Monsanto Fault was evaluated. This evaluation applied the analytical solution of the advective dispersion equation for a planar source presented in Domenico and Schwartz (1990) (Equation 3). This equation solves for the maximum plume concentration at a specified distance from a planar source.

$$C_{\text{max}} = C_0 erf \left[ \frac{Y}{4(\alpha_y x)^{1/2}} \right] erf \left[ \frac{Z}{4(\alpha_z x)^{1/2}} \right]$$
 (Equation 3)

Where:

C<sub>0</sub> is the source zone concentration;

Y is the source width;

Z is the source depth;

 $\alpha_y$  is the transverse horizontal dispersivity; and,

 $\alpha_z$  is the transverse vertical dispersivity.

The decline in peak chloride concentrations between TW-37, TW-20 and TW-53 were evaluated to estimate dispersivity. A C<sub>0</sub> value of 275 mg/L was assumed, representative of peak chloride concentrations at TW-37. The source width was estimated at 430 feet (132 meters), equivalent to the width of the Underflow Solids Ponds. The depth of the source was assumed equal to 30 feet (9 meters). Values of transverse horizontal and transverse vertical dispersion were changed until C<sub>max</sub> was equivalent to peak measured chloride concentrations at TW-20 (190 mg/L) and TW-53 (120 mg/L) located 4,000 feet and 4,890 feet downgradient of the source, respectively. Because this method involved estimation of two variables in Equation 3, the solution is not unique. This calculation also assumes TW-20 and TW-53 are sampling the core of the chloride plume. Despite these limitations, this exercise was useful in confirming that applied values of dispersivity in the GoldSim model were appropriate with respect to site observations.

The results of this evaluation are summarized below. Complete calculations are provided as Attachment A. In the Table below, longitudinal dispersivity ( $\alpha_i$ ) is assumed equal to 10% of the distance traveled. These results suggest that the assumed values for dispersivity applied in the GoldSim model are reasonable.

<u>TABLE 8</u>
Results of Dispersivity Evaluation

Parameter	TW-20	TW-53
Peak Measured Chloride Concentration	190 mg/L	120 mg/L
Distance From Source (TW-37)	1,220 m	1,490 m
Assumed Transverse Horizontal Dispersivity	1.2 m	3.0 m
	1% αι	2% αι
Assumed Transverse Vertical Dispersivity	0.01 m	0.01 m
	0.01% αι	0.01% αι
Calculated Peak Chloride Concentration	191 mg/L	116 mg/L

Transport Model Results

The GoldSim model simulated transport for a period of 100 years. Two hundred realizations were conducted. Groundwater flow was simulated as pipe flow. To incorporate transverse dispersion, the plume function was applied.

Because the model assumes a constant source, upon reaching steady state, constituent concentrations remain constant. Peak predicted COC concentrations at the compliance point are summarized in Table 9. Constituents predicted to exceed remediation goals are highlighted in bold type. Both selenium and cadmium are predicted to exceed compliance levels. Although manganese from the Northwest Pond is predicted to exceed the remediation goal, provided conditions in the Upper Basalt Zone are oxidizing, manganese concentrations may in fact remain below the remediation goal due to precipitation of manganese oxides and hydroxides.

<u>TABLE 9</u>
Predicted Compliance Point Concentrations

Constituent of Concern	uent of Remediation		n Compliance Point ntration g/L)
(COC)	(mg/L)	Northwest Pond	Old Hydroclarifier
		Source	Source
		<0.001 to 0.32	0.08 to 0.52
Cadmium (Cd)	0.005	94% probability of	100% probability of
		exceedence	exceedence
Fluoride (F)	4	1.5	1.3
Nitrate (as N) (NO3)	10	2.8	3.2
Selenium (Se)	0.05	0.13	0.27
Manganese (Mn)	0.18	1.2	0.02

With respect to selenium transport, the GoldSim model results are consistent with selenium behavior west of the Monsanto Fault. Selenium concentrations in the fence line wells west of the fault (TW-39 and TW-10) currently exceed the remediation goal. In 2001, selenium concentrations in TW-39 and TW-10 were 0.2 mg/L. Peak source zone selenium concentrations in TW-37 and TW-40 are comparable at 1.2 mg/L (1991) and 1.3 mg/L (2000), respectively. One would therefore expect that in the future, if operations of the pumping wells are ceased, selenium concentrations in TW-12 would rise to levels above the remediation goal.

Cadmium concentrations in TW-39 also currently exceed the remediation goal (0.016 mg/L in 2001). It is therefore reasonable to assume that if operation of the pumping

wells is ceased, cadmium concentrations in TW-12 will rise to levels above the remediation goal. Because source zone cadmium concentrations in TW-40 are elevated in comparison to TW-37, exceedences are likely inevitable. It should be noted that determination of site-specific  $K_d$  values for cadmium would improve the model estimates of cadmium transport.

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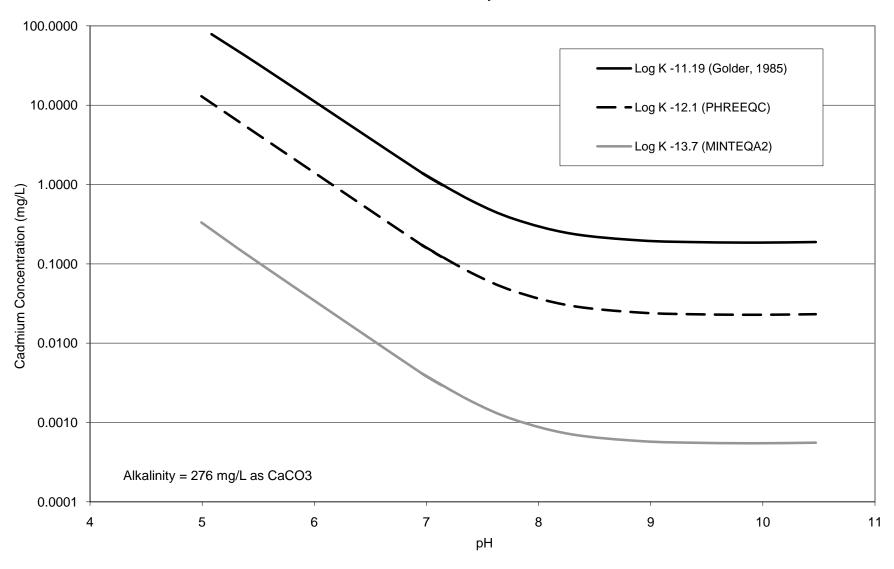
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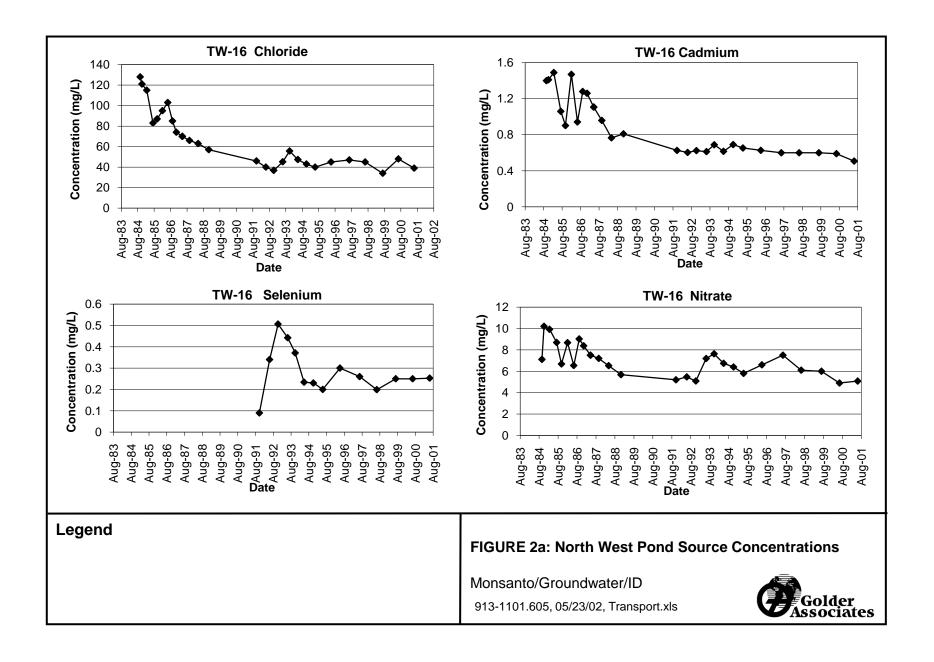
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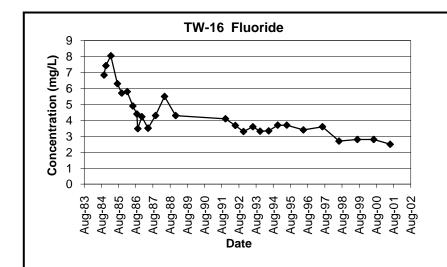
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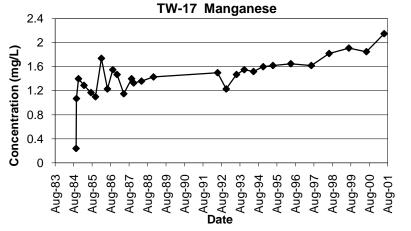
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FIGURE 1
Otavite Solubility Curves







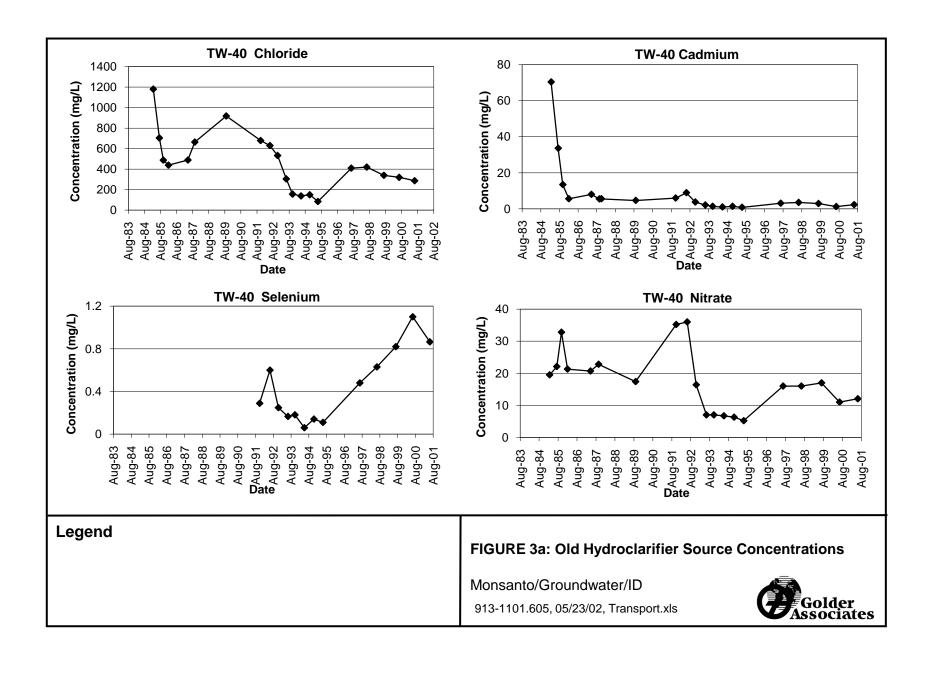


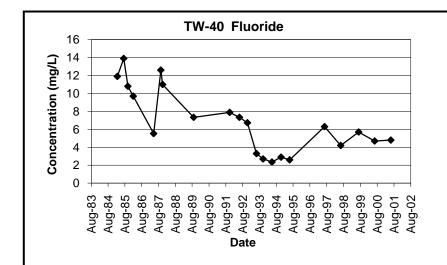
# Legend

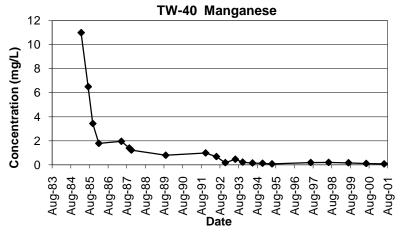
**FIGURE 2b: North West Pond Source Concentrations** 

Monsanto/Groundwater/ID 913-1101.605, 05/23/02, Transport.xls









Legend

FIGURE 3b: Old Hydroclarifier. Source Concentrations

Monsanto/Groundwater/ID 913-1101.605, 05/23/02, Transport.xls



FIGURE 4
TW-40 Cadmium Versus pH

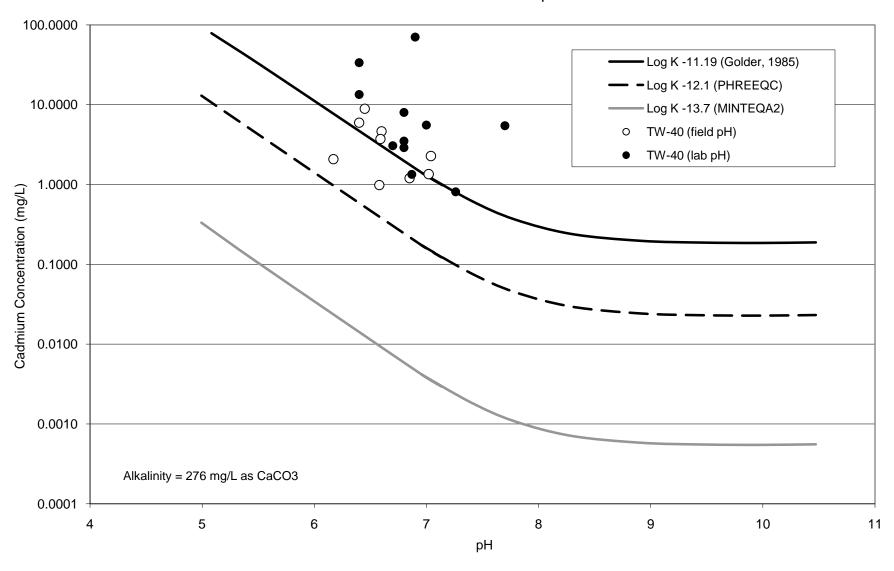


FIGURE 5
TW-37 Cadmium Versus pH

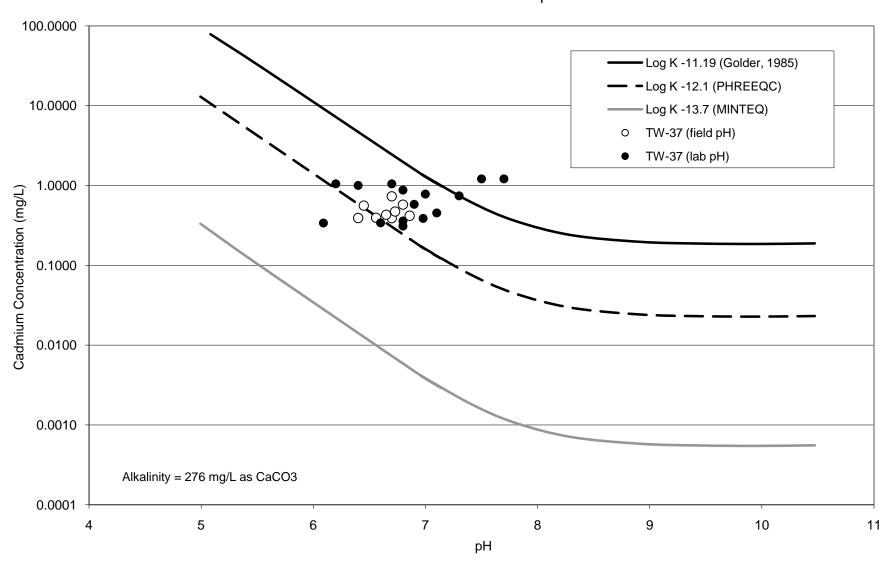
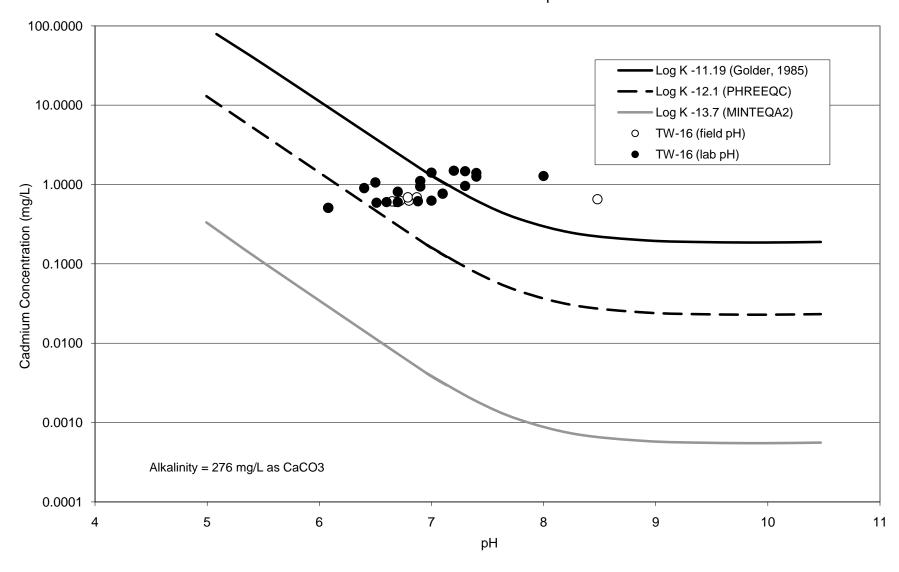


FIGURE 6
TW-16 Cadmium Versus pH



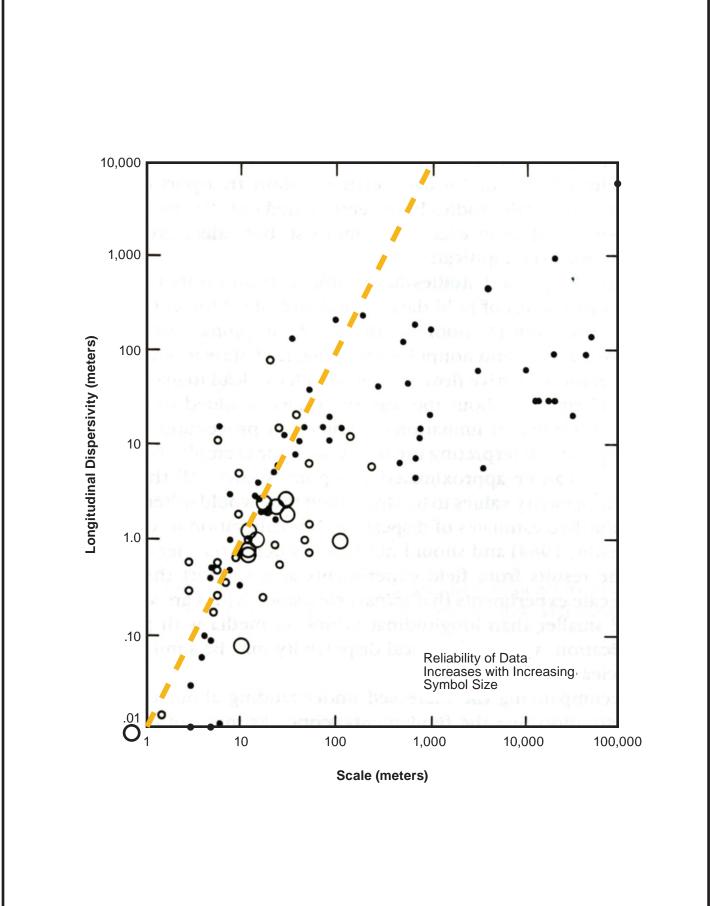


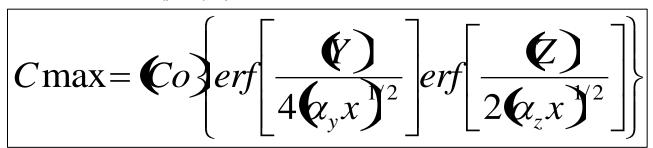
FIGURE 7
SCALE DEPENDENCE OF DISPERSIVITY
MONSANTO/RI/FS/IDAHO

Reference: Gelhar et.al. 1985

## ATTACHMENT A

**Dispersivity Calculations** 

## Dominico and Schwartz (p. 645) Equation 17.16



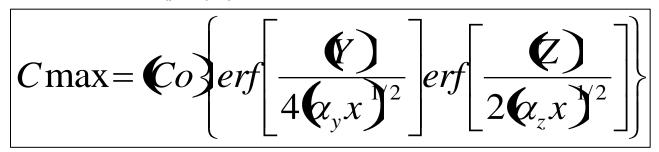
## Chloride from Old Underflow Solids (TW-37 to TW-20)

CI	275 mg/L	
x (length)	1220 m	Distance from source to compliance point
alpha l	122 m	Longitudinal dispersivity is 10% of path length
alpha y	1.2 m	Transverse dispersivity is 1% of longitudinal dispersivity
		Transverse dispersivity is 0.01% of longitudinal dispersivity (assume dispersion in z direction is negligible due to
alpha z	0.01	impermeable zone)
Υ	130 m	source width (Old Underflow Solids)
Z	9.1 m	source depth (full depth of aquifer = 30 feet)

# Solve for C<sub>max</sub> (should equal peak at TW-20 - 190 mg/L)

Α	Со	275 mg/L	
B	Y	130 m	$C = A \} erf \left[ \frac{C}{C} \right] erf \left[ \frac{C}{K} \right]$
C	4(a <sub>y</sub> x) <sup>1/2</sup>	154 m	
D	B/C	0.84	
E	erf D	0.77	
F	Z	9.1 m	$C = (A) \{ rf(D)erf(G) \}$ $C = A \{ *H \}$
K	2(a <sub>z</sub> x) <sup>1/2</sup>	8 m	
G	F/K	1.19	
H	erf G	0.91	
I	E * H	0.69	
J	A * I	191 mg/L	

## Dominico and Schwartz (p. 645) Equation 17.16



## Chloride from Old Underflow Solids (TW-37 to TW-53)

CI	275 mg/L		
x (length)	1490 m	Distance from source to compliance point	
alpha l	149 m	Longitudinal dispersivity is 10% of path length	
alpha y	3.0 m	Transverse dispersivity is 2% of longitudinal dispersivity	
		Transverse dispersivity is 0.01% of longitudinal dispersivity (assume dispersion in z direction is negligible due to	
alpha z	0.01	impermeable zone)	
Υ	130 m	source width (Old Underflow Solids)	
Z	9.1 m	source depth (full depth of aquifer = 30 feet)	

# Solve for C<sub>max</sub> (should equal peak at TW-53 - 120 mg/L)

Α	Со	275 mg/L	
В	Υ	130 m	$C = A $ $erf$ $  \Psi  _{erf}   \Psi  _{erf}$
С	$4(a_{y}x)^{1/2}$	267 m	$ C  = \{A \mid ert \mid - ert \mid - \}$
D	B/C	0.49	
_			
E	erf D	0.51	
F	Z	9.1 m	$C = (A) \{ rf(D) erf(G) \}$
K	$2(a_z x)^{1/2}$	9 m	$C = (A) \operatorname{erf}(D)\operatorname{erf}(G)$
G	F/K	0.97	
Н	erf G	0.83	
ı	E * H	0.42	$C = A + E * H + \sum$
•	2	0.12	
J	A * I	116 mg/L	